

AD-A038 139

ROYAL AIRCRAFT ESTABLISHMENT FARNBOROUGH (ENGLAND)  
MECHANICAL SHEAR DEGRADATION OF POLYMERS IN SOLUTION: A REVIEW.(U)  
JUN 76 J KNIGHT

F/6 7/3

UNCLASSIFIED

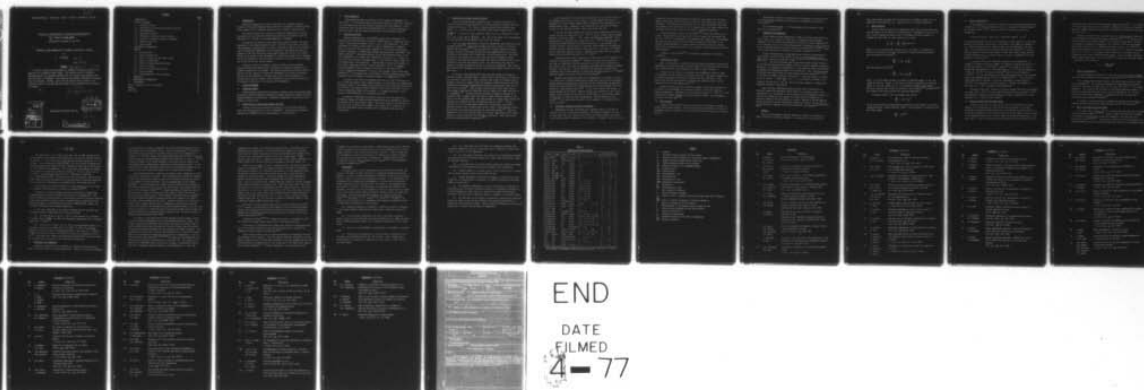
RAE-TR-76073

DRIC-BR-53365

NL

| OF |

AD  
A038139



END

DATE  
FILMED  
4-77

ADA 038139

TR 76073

JUNE  
1976



Crown Copyright  
1976

COPYRIGHT ©

CONTROLLER HMSO LONDON  
1976

DDC FILE COPY

UNLIMITED

BR53365 ✓

ROYAL AIRCRAFT ESTABLISHMENT  
TECHNICAL REPORT 76073



**MECHANICAL SHEAR  
DEGRADATION OF POLYMERS  
IN SOLUTION: A REVIEW**

by

J. Knight

DDC  
RECEIVED  
APR 7 1977  
D

*[Handwritten signature]*

PROCUREMENT EXECUTIVE MINISTRY OF DEFENCE  
FARNBOROUGH HANTS

ROYAL AIRCRAFT ESTABLISHMENT

Technical Report, 76073

Received for printing 12 June 1976

MECHANICAL SHEAR DEGRADATION OF POLYMERS IN SOLUTION: A REVIEW.

by

J./Knight

11 Jun 76

12 34p.

SUMMARY

14 RAE-TR-76073

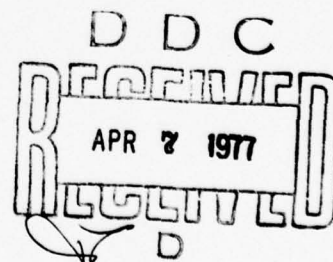
A review is given of the breakdown of polymers in solution caused by the application of mechanical shear energy. The characteristics of different degrading devices are mentioned together with the factors which determine the rate and extent of breakdown. The energetics and possible mechanisms of degradation are discussed. Finally, a more critical overall view is given of the results in order to list the conclusions which can be supported by the majority of evidence.

18 DRIC

19 BR-53365

White Section		<input checked="" type="checkbox"/>
Buff Section		<input type="checkbox"/>
RECEIVED		<input type="checkbox"/>
DISTRIBUTION/RELIABILITY CODES		
SPECIAL		
A		

Departmental Reference: Mat 291



310450

Approved for public release;  
Distribution Unlimited

CONTENTS

	<u>Page</u>
1 INTRODUCTION	3
2 TYPES OF DEGRADER	3
2.1 Mechanical shaker	3
2.2 Mastication of concentrated polymer solutions	3
2.3 Pump degradation	4
2.4 High-speed stirrers	4
2.5 Capillaries, nozzles, jets and sinters	5
2.6 Concentric cylinder rotational viscometers	6
2.7 Turbulent pipe flow	7
2.8 Other methods	7
3 ASSESSMENT OF DEGRADATION	8
4 RESULTS	8
4.1 Rate equations	9
4.2 Onset of degradation	10
4.3 Effect of shear rate and shear stress	10
4.4 Effect of temperature	11
4.5 Effect of initial molecular weight	11
4.6 Effect of solvent	12
4.7 Effect of polymer concentration	12
4.8 Type of polymer	13
4.9 Interdependence of shear variables	13
5 ENERGETICS	14
6 MECHANISMS OF DEGRADATION	15
7 CONCLUSIONS	18
Table 1 Examples of shear conditions	20
Symbols	21
References	22



## 1 INTRODUCTION

Mechanical degradation in this review refers to a chemical scission reaction of the polymer backbone which results in a decrease in molecular weight of the polymer with a consequent decrease in the viscosity of the solution.

This Report reviews the literature on mechanical degradation of polymer solutions up to June 1975 and includes work which has been reported since the publication of a review<sup>1</sup> on the mechanochemistry of polymers.

The need for the present review arises from interest at RAE on the shear degradation of anti-misting additives used in aircraft safety fuels, the latter being designed to suppress fire in a crash. One area of concern is the minimising of unintentional degradation of that fraction of the safety fuel which is returned to the fuel tanks after being pumped around the aircraft fuel system. Another major problem is the achievement of a sufficiently high level of degradation of the additive in the fuel stream to enable it to pass efficiently through the filters of the fuel control system.

Accounts of some of the papers listed are limited to their Chemical Abstracts summary and papers wholly concerned with ultrasonic degradation of polymer solutions are not included. The results obtained by different investigators on certain aspects of mechanical degradation are at times conflicting but they are all mentioned in the main text; a more critical appraisal is deferred until section 7 where a list is drawn up of the conclusions which can be supported by the work of the majority of investigators.

## 2 TYPES OF DEGRADER

### 2.1 Mechanical shaker

Flasks partially filled with solutions of polymers such as poly(isobutylene) [PIB] and polystyrene [PS] were mechanically shaken, producing vigorous continual splashing against the flask walls. Significant degradation occurred only after shaking for many hours<sup>2</sup>.

### 2.2 Mastication of concentrated polymer solutions

Various polymers were treated with solvents to form swollen masses and these were then masticated in an inert atmosphere<sup>3</sup>. Solutions of poly(methyl methacrylate) [PMMA] have also been degraded in a vibratory mill<sup>4</sup>.

### 2.3 Pump degradation

A power-shearing pump test has been used to assess the degradation of motor oils<sup>5</sup>. A vane pump was used to shear power-transfer fluids<sup>6</sup> and a hydraulic test rig, based on an aircraft hydraulic pump has also been employed<sup>7</sup>. Polyisobutylene (PIB) solutions were pump-degraded with a jet-thrust appliance in which the thrust tube was mounted on the frame of an analytical balance<sup>8</sup>.

### 2.4 High-speed stirrers

Aqueous poly(methacrylic acid) [PMA] solutions were degraded by the propellers of a Waring blender rotating at 12000rev/min in a cooled steel container. Cavitation was thought to play a part in the degradation<sup>9</sup>. An ultra high-speed air turbine stirrer, able to rotate at 80000rev/min (12500cm/s blade tip velocity), has been used to degrade PS<sup>10</sup> and Virtis homogenisers, working at speeds up to 45000rev/min degraded deoxyribonucleic acid (DNA)<sup>11</sup> and organic polymers<sup>12</sup>. Harrington employed special thin sharpened blades on his Virtis homogeniser and assumed that degradation occurred only in a region of high shear rate extending a distance equal to the molecular contour length from the leading edge of the propeller<sup>13</sup>. Hydroxy-ethyl cellulose was degraded at 70°C using a high-shear stirrer<sup>14</sup>, whilst polystyrene (PS) in cyclohexane suffered degradation after stirring for 20 hours at a low shear rate<sup>15</sup>. Fujiwara studied the degradation of various vinyl polymers using a high-speed homogeniser<sup>16-19</sup> and Minoura has recently made a detailed examination of polymer degradation using a homomixer rotating at speeds up to 30000rev/min<sup>20-26</sup>.

A variant on the action of high-speed stirrers is a rig<sup>27</sup> consisting of a pair of identical wheels, each of which rotates at a fixed speed in a mechanically unconnected casing. The casings contain polymer solution and solvent respectively and rotation of the wheels produces turbulent flow of the fluids which in turn produces measurable torques on the casings. In a similar appliance, a disc rotates at 700-11000rev/min in a thermostatted cell<sup>28</sup>.

The method of high-speed stirring can generally only give qualitative information because the amount of shear depends both on the geometrical form of the stirrer and of the container vessel. The overall kinetics are controlled by such factors as the motor speed, sample, vessel shape (as it influences the efficiency with which fluid is directed onto the blades), blade shape and concentration.

## 2.5 Capillaries, nozzles, jets and sinters

A more controlled method of applying shear to polymer solutions is to force the solution through capillaries or orifices either at constant flow rate (constant shear rate,  $\dot{\gamma}$ ) or under a constant pressure head (constant shear stress,  $\tau$ ). The shear rate in a capillary varies from a maximum value of  $\frac{4}{\pi r^3} \frac{dV}{dt} \text{ s}^{-1}$  at the wall to zero along the centre line for a capillary of radius  $r$  cm with a flow rate of  $\frac{dV}{dt} \text{ cm}^3/\text{s}$ . Not only is the shear field inhomogeneous but the capillary entrance geometry can affect the results.

Since the first experiments on capillary degradation using capillaries with platinum nozzles<sup>29-31</sup>, Bestul and coworkers have done a series of controlled laminar-flow experiments<sup>32-39</sup> using a capillary of length 0.635cm and radius 0.019cm. The disc containing the capillary was clamped between two collinear cylindrical steel tubes, each of which had a close-fitting piston. The piston was used to force material at a fixed flow rate into the opposite cylinder through the capillary and successive passes were made by alternating the pistons which were driven back and forth by a cam. For every other pass, the force required to produce the given flow rate of solution was measured. These experiments measured the variation in initial load (and hence shear stress) for a fixed shear rate.

In contrast, other workers have fixed the shear stress by forcing the solution through a capillary under a constant head of gas pressure and looked at the variation of shear rate. Thus, solutions were forced by nitrogen pressure through a capillary of length 7.65cm and diameter 0.033cm joining two identical thermostatted vessels and temperature and pressure readings were taken at both ends of the capillary<sup>40</sup>. Also, polymer solutions were forced under laminar flow through a capillary of 0.04cm bore and 1cm length at nitrogen pressures up to  $140\,000 \text{ kg/m}^2$ <sup>10</sup>. Turbulent flow was obtained by passage of aqueous polyacrylamide (PAA) through a steel capillary of length 38cm and diameter 0.15cm under a constant pressure head. The timed passage of a known volume through the capillary was compared with the corresponding time for water<sup>41</sup>. Toluene solutions of PS were forced under laminar flow through glass capillaries of diameter 0.025cm, with a 0.020cm brass orifice, under a fixed nitrogen pressure. The pressure drop across the capillary was accurately measured<sup>42</sup>. Capillary degradation even at the low wall shear rate of  $180 \text{ s}^{-1}$  was observed after 28000 passes of a toluene solution of PS through a capillary<sup>43</sup>. Many other workers have also studied capillary degradation<sup>44-51</sup>.



In one experiment<sup>40</sup>, the variation in capillary diameter had no effect on the degradation for a given stress, whilst in another paper<sup>42</sup> the extent of degradation at shear stresses between 800 to 1750 dyn/cm<sup>2</sup> was independent of the length:diameter ratio, suggesting that degradation was caused by the higher stresses at the capillary entrance, rather than within the tube.

A jet made by almost sealing off a piece of Pyrex tubing was tested<sup>52</sup> with various oils up to a shear rate of  $3.9 \times 10^5 \text{ s}^{-1}$ , and was further used to degrade polymers of molecular weight  $1 \times 10^5$ . Morris and Schnurmann reported<sup>53</sup> that a high-pressure jet operating up to shear rates of  $1 \times 10^7 \text{ s}^{-1}$  broke down polymers of molecular weight 25000 but few details were given. It was claimed that tetralin solutions of polyethylene of molecular weight 27000 were degraded when expelled through a 0.042cm nozzle at pressures of  $2.1 \times 10^7$  and  $4.2 \times 10^7 \text{ kg/m}^2$  onto a crash plate immersed in water. Degradation increased when the distance between nozzle and plate was short (0.2 to 1.0cm)<sup>54</sup>.

A standard diesel injector operating at shear rates of  $10^7 \text{ s}^{-1}$  degraded oil solutions of unspecified polymers<sup>55</sup>. Degraded solutions were automatically recycled, the temperature rose during operation to 40°C and the nozzle was of the 'pintle' type. The extent of degradation decreased with decreasing breaking pressure on the spring. A similar appliance has been used to degrade polysiloxanes using a nozzle diameter of 0.024cm and breaking pressure  $1.4 \times 10^6 \text{ kg/m}^2$ . Different nozzles and rates of flow have been employed<sup>56</sup>.

Mineral oils containing polymer were degraded both by a needle valve and by a metal sieve containing 0.06cm holes through which the solution was pumped<sup>57</sup>. Similar devices include a plate containing circular perforations through which a PAA solution was forced<sup>58</sup> and a Pyrex sintered disc of pore diameter 14 microns, mounted in a high-pressure gas cell<sup>10</sup>. In this case, however, the polymer became adsorbed on the sinter, causing blockage and a reduction in pore size<sup>59</sup>. Another device related in its action to the capillary is the all-glass atomiser normally used for spraying paper chromatograms. DNA was degraded in this device<sup>60,61</sup>; the results were dependent on the geometry of the atomiser and on the air pressure.

## 2.6 Concentric cylinder rotational viscometers

Undoubtedly the most controlled way of applying shear to a polymer in solution is to use a rotational viscometer. The normal arrangement consists of an inner rotor and outer stator, both of which are thermostatted. The torque on the outer cylinder is measured at a fixed speed of rotation. The use of narrow



clearances in the annular gap between cylinders ensures laminar flow and when highly concentrated viscous polymer solutions are used, high shear stresses are attainable. Both shear stress and shear rate are readily measurable and these are uniform for the whole solution if the annular gap is very small, making this instrument the best one to use for the study of degradation kinetics.

Johnson performed a series of experiments<sup>62-68</sup> using 10% PIB solutions in cetane. The cylinders were 4.5cm long, 2.5cm in diameter and the annular gap was  $7.5 \times 10^{-4}$  cm. In one paper<sup>67</sup>, the viscometer was fitted with a flow-through attachment so that solution could be slowly syringed into the middle of the annulus, became degraded to a limiting molecular weight in about two seconds, and was then collected at the ends of the cylinders. Other workers have used the same apparatus<sup>2</sup>.

A number of other papers<sup>69-76</sup> also describe degradation in rotational viscometers.

## 2.7 Turbulent pipe flow

Most of the studies in capillaries and rotational viscometers concerned the degradation of polymer solutions of greater than 0.1% concentration under laminar flow conditions, where some estimate may be made of shear variables.

Polymers such as PAA and poly(ethylene oxide) [PEO] are useful in lower concentrations as drag reducers in turbulent pipe flow. The shear variables are not readily calculable here and so the results are only qualitative. Many workers have studied the degradation caused by the turbulent flow of dilute aqueous solutions through smooth pipes<sup>77-92</sup>.

Organic solutions have been similarly degraded. Thus PIB in kerosine and in mineral oil was degraded in a circulation system in which the fluid was pumped through pipes. Degradation from a molecular weight of  $5 \times 10^6$  to  $0.4 \times 10^6$  occurred while passing through a centrifugal pump for 15min. Less degradation occurred at the gear pump<sup>93,94</sup>.

## 2.8 Other methods

A special device has been used to force fluid at high pressure through the narrow annular region between a close-fitting piston and cylinder. The extent of degradation greatly increased after lateral grooves had been scored on the piston surface<sup>10</sup>.

When polymer solutions were agitated in the presence of solid particles, the polymers became adsorbed on the particles and degradation occurred by collisions<sup>95,96</sup>.

PS of molecular weight  $1 \times 10^7$  was degraded in the columns of a gel permeation chromatograph<sup>97</sup>.

### 3 ASSESSMENT OF DEGRADATION

Several papers express degradation in terms of directly observable parameters such as the reduction in flow time of a polymer solution through a capillary<sup>43</sup> or the decrease in sedimentation coefficient for DNA degradation<sup>98</sup>. In the turbulent flow of solutions through pipes, degradation is often expressed as the percentage reduction in drag-reducing effectiveness<sup>78,79,82,83,85</sup>, whilst other workers measured the reduction of solution viscosities<sup>9,53,55,56</sup>.

In most investigations, the degradation was followed by measurement of the intrinsic viscosity of the polymer and use of the Mark-Houwink relation ( $[\eta] = CM^\alpha$ ) to compute the molecular weight<sup>2,3,10,13,19-22,24-26,35-40,42,44-46,62,63,72,93</sup>. The values obtained, and the molecular weights quoted in Table 1, are viscosity-average molecular weights and they can give a somewhat misleading impression of the progress of degradation if the molecular weight distributions of degraded and undegraded polymer are very different. Thus, viscosity-average values have been used in place of number-average molecular weights<sup>26,35,36,38</sup> to calculate the number of moles of scissions,  $n$ , per unit volume of solution using the formula  $n = w\left(\frac{1}{M} - \frac{1}{M_0}\right)$ , where  $w$  is the weight of polymer in unit volume of solution and  $M$  and  $M_0$  are the molecular weights of degraded and undegraded material, respectively.

Apart from DNA, undegraded polymers normally have a distribution of molecular weights and degradation often results in a different form of this distribution. For this reason, a clearer picture of the degradation reaction is obtained by studying not just changes in average molecular weights but by observing changes in the distribution as a whole. Batches of 500-600 degraded polymer molecules have been individually measured by electron microscopy<sup>41</sup> but the technique most commonly used was gel permeation chromatography<sup>8,15,65-67,76,80,97</sup>.

### 4 RESULTS

There is wide agreement that the shearing of polymers in solution can cause a reduction in molecular weight at a rate which is at first rapid but

then progressively decreases with increasing time or number of passes until it approaches a limiting value  $M_L$ , characteristic of the shear conditions.

#### 4.1 Rate equations

Several workers found that the degradation data fitted a first-order rate law with respect to the number of cleavable bonds. Harrington<sup>10</sup> stated that the rate of bond breakage was proportional to the number of bonds available for breakage and this leads to a rate equation of the form

$$\frac{1}{M} - \frac{1}{M_L} = \left( \frac{1}{M_0} - \frac{1}{M_L} \right) \exp(-kt) ,$$

where  $k$  is the scission rate constant and  $t$  the time. In degradation of 2-5% (w/v) solutions by stirring, the results<sup>21</sup> fitted both the first-order rate law proposed by Jellinek<sup>99</sup>,

$$\frac{dn_M}{dt} = k(M - m) \frac{n_M}{m} ,$$

and that proposed by Allen<sup>100</sup>,

$$\frac{dn_M}{dt} = k(M - M_L) \frac{n_M}{m} ,$$

where  $n_M$  is the number of moles of polymer of molecular weight  $M$  per unit volume of solution,  $dn_M/dt$  is the rate of scission of molecules of molecular weight  $M$  per unit volume, and  $m$  is the molecular weight of the monomer. The latter equation also fitted the results of other workers<sup>25,26</sup> and Bestul<sup>36,38</sup> also assumed first-order kinetics for capillary degradation.

In another paper<sup>19</sup>, the rate equation was given as

$$-\frac{dM}{dt} = k(M - M_L)^2$$

and it was postulated that degradation was affected by the presence of adjacent polymer molecules. During turbulent flow<sup>28</sup>, a rate equation of a different form was found, namely

$$\frac{dM}{dt} = kM^{(\alpha+1)} .$$

#### 4.2 Onset of degradation

In the degradation of poly(vinyl acetate) it was claimed that degradation started not in the polymer backbone but in ester linkages at the branch points<sup>17</sup>. The following simple rule<sup>101</sup> was put forward for predicting the start of degradation:

$$\text{solution viscosity} \times \text{shear rate} \times (\text{molecular weight})^2 \geq 10^{14}.$$

It was postulated that the shear rate necessary to cause rupture of a long chain molecule was inversely proportional to the square of the number of segments in it. Hence very high molecular weight polymer could be degraded at low shear rates. The extending forces on polymer molecules were thought<sup>102</sup> to increase with the square of the molecular length, so that under stress longer molecules ruptured preferentially. In another paper, the onset of degradation was independent of concentration<sup>87</sup>.

As a guide to the shear conditions necessary to start degradation of polymers of different molecular weights, the following examples are given. PIB of molecular weight  $2.3 \times 10^6$  began to degrade<sup>103</sup> at a shear rate of  $156 \text{ s}^{-1}$ , whereas the same polymer with a molecular weight of  $8 \times 10^5$  was not degraded at a shear rate of  $10^4 \text{ s}^{-1}$  but began to degrade<sup>63</sup> when this was increased to  $3 \times 10^5 \text{ s}^{-1}$ . For the same material, the minimum necessary value of the parameter shear stress/temperature was found<sup>67</sup> to be  $60 \text{ dyn/cm}^2 (\text{K})^{-1}$ . PIB of molecular weight 50000 was not degraded in capillary experiments at shear rates of  $10^5$ – $10^6 \text{ s}^{-1}$ , but material of molecular weight  $2 \times 10^6$  began to degrade<sup>94</sup> at a shear rate of  $6 \times 10^5 \text{ s}^{-1}$  and shear stress  $2000 \text{ dyn/cm}^2$ .

According to Morris<sup>53</sup>, polymers of molecular weight 25000 were not degraded at a shear rate of  $10^5 \text{ s}^{-1}$  but were broken down when this was increased to  $10^7 \text{ s}^{-1}$ . Polysiloxanes of molecular weight 57000 did not begin to degrade until a shear threshold of  $8 \times 10^5 \text{ dyn/cm}^2$  was reached<sup>56</sup>.

#### 4.3 Effect of shear rate and shear stress

As noted in section 4.2, there appears to be some relationship, though perhaps not a well-defined one, that as the molecular weight of a polymer decreases, progressively higher shear rates are necessary to cause scission. In a capillary experiment it was found that the ratio of the number of bond ruptures to the molecular weight after a certain number of passes was proportional to the shear rate<sup>49</sup>. Other investigations with capillaries have also indicated that an



increase in shear rate gave larger molecular weight reductions<sup>34,51</sup>. An increase in the rotor speed of a stirrer from 10000 to 30000 rev/min lowered the limiting molecular weight, showing that the extent of degradation increases with increasing shear rate<sup>21</sup>.

However, the shear *stress*, not shear rate, was said by several workers to be the parameter controlling the extent of degradation<sup>10,62,65,67</sup> and this view is supported by the following example<sup>76</sup> for a polymer solution whose viscosity was changed by changing the temperature: the solution at 40°C did *not* degrade under a shear stress of  $1.2 \times 10^4$  dyn/cm<sup>2</sup> and shear rate of  $1.15 \times 10^5$  s<sup>-1</sup> but degradation did occur at 25°C with a shear stress of  $1.43 \times 10^4$  dyn/cm<sup>2</sup> and shear rate of  $4.2 \times 10^4$  s<sup>-1</sup>. An increase in shear stress gave an increased rate of degradation and a lower limiting molecular weight. Also, the highest molecular weight present after shear,  $M_c$ , was found<sup>40</sup> to be related to the shear stress,  $\tau$  (dyn/cm<sup>2</sup>), by the relation

$$M_c = \frac{3.59 \times 10^8}{\tau^{(0.41)}} .$$

#### 4.4 Effect of temperature

For many degraders operating at a fixed shear rate, the extent of degradation was found to decrease with increasing temperature<sup>3,12,34,35,40,65,73,76,85</sup>.

For a constant shear *stress*, however, temperature variation had no effect on the degradation<sup>40</sup>. No temperature dependence of degradation was observed either in a concentric cylinder device in the range -50° to 0°C<sup>71</sup> or in a glass atomiser<sup>61</sup>. In a study of the variation of the limiting molecular weight,  $M_L$ , with shear stress and with shear rate at various temperatures, the  $M_L$ -shear stress relationship was independent of temperature but the  $M_L$ -shear rate relationship was temperature dependent<sup>62</sup>.

In contrast to the above results, degradation increased with increasing temperature when solutions were passed through nozzles<sup>54</sup> and capillaries<sup>44</sup>.

#### 4.5 Effect of initial molecular weight

For a given rate of shear, the rate of degradation increased with increasing initial molecular weight<sup>2,3,40,80,94</sup>. Several workers also found that polymers of different initial molecular weight were degraded to the same limit for a given shear stress<sup>3,26,40,62</sup>. In two cases, different limits were obtained, but these apparently conflicting results may have been caused by the inadequacy of the

viscosity-average molecular weight results to describe the course of degradation for polymers of different polydispersity<sup>21,34</sup>.

The applied shear may often be insufficient to cleave all the molecules making up the initial distribution of molecular weight, and, in this case, only those molecules having a chain length greater than a certain critical value will rupture, leading to a narrowing of the distribution<sup>11,19,37,55,61,76,80</sup>.

#### 4.6 Effect of solvent

The degree to which polymer chains are expanded in a solution depends on the nature of the solvent. The so-called 'poor' solvents give solutions of low intrinsic viscosity in which the polymer coils are relatively unexpanded and here there are quite strong polymer-polymer interactions. 'Good' solvents give solutions in which the polymer coils are well expanded. Several workers have found that polymers degrade to a greater extent in poor solvents than in good solvents, other variables being equal<sup>10,12,19,21,24,25,46,51,88</sup>. In degradation by mechanical agitation in flasks, the more viscous solutions of PIB in cyclohexane showed less degradation than the less viscous toluene solutions under similar conditions; degradation in toluene was similar to that in decalin<sup>2</sup>.

Other investigations showed that the solvent quality had little effect on degradation either at high<sup>104</sup> or low<sup>19</sup> concentrations and a series of polymer degradations in mixed solvents indicated that solvent composition had little effect on the degradation rate<sup>44-46</sup>.

In one account using dilute solutions, degradation was more extensive in good solvents<sup>26</sup>.

There was no obvious correlation between rate of degradation and other properties of solvents such as vapour pressure, heat of vaporisation or density<sup>25</sup>. Indeed, the use of volatile solvents such as hexane did not markedly alter the degradation rate, suggesting that cavitation did not play any important part in these cases<sup>28,37</sup>.

#### 4.7 Effect of polymer concentration

Numerous papers describe the influence of changes in polymer concentration on the extent and rate of degradation. The results appear to be conflicting and may be different for different ranges of concentration, making comparisons difficult.

The degradation by stirring of PEO and PMMA at different concentrations covering 1 to 5% (w/v) showed that the extent of degradation, expressed as the number of scissions per molecule, was independent of concentration in this range<sup>21-23</sup>. A similar result was obtained for capillary degradation of PS and PIB in the range 5-20%<sup>38,51</sup>.

In the concentration range 0.04-2%, the rate of degradation of PS and PMMA in various solvents was higher and  $M_L$  lower as the concentration decreased, this being especially marked for concentrations lower than 0.5%<sup>26</sup>. Moreover, the effect of concentration on  $M_L$  was large for good solvents but small for poor ones, in contrast to earlier work at higher concentrations<sup>25</sup>. In other degradation experiments by stirring, the extent of degradation increased with decreasing concentration<sup>17,49</sup> and a similar trend was found for other degraders<sup>2,83,104</sup>. For a given stress, the limiting molecular weight decreased with decreasing concentration<sup>40</sup>. At constant shear rate, more concentrated solutions exhibited more degradation but at constant stress, they showed less degradation<sup>63</sup>.

In contrast, other workers found a decrease in extent of degradation with decreasing concentration<sup>28,34,38,76</sup>.

During the mastication of swollen gels, degradation decreased rapidly with an increase in the proportion of solvent<sup>3</sup>.

#### 4.8 Type of polymer

Many polymers have been studied, both in organic and aqueous solution. PIB was studied most because of its reluctance to undergo branching or crosslinking reactions.

Polysiloxanes are more resistant to degradation than vinyl polymers because of their stronger silicon-oxygen bonds in the polymer backbone and because of their greater flexibility<sup>56</sup>.

#### 4.9 Interdependence of shear variables

Most of the variables mentioned in sections 4.3 to 4.8 cannot be individually changed without affecting others. Thus the effects of temperature, initial molecular weight and concentration on degradation could be regarded simply as a result of their effect on solution viscosity. At a constant shear rate, a decrease in temperature or an increase in initial molecular weight or concentration leads to a higher viscosity, a higher shear stress and consequently more degradation<sup>76</sup>. However, this simple interpretation of the experimental results may not be a

sufficiently accurate one. The limiting molecular weight obtained for a given stress *does* vary slightly with temperature and concentration and the variation has been described in terms of the reduced variables stress/temperature and stress/(temperature  $\times$  volume fraction of polymer)<sup>63,65,67</sup>.

The various effects of initial molecular weight, concentration and temperature on the degradation have been combined<sup>10</sup> in a single parameter representing the average force per molecule needed to degrade it to its final state. The force  $f_c$  was calculated from the expression

$$f_c = \frac{(\eta_L - \eta_s)\dot{\gamma}}{nz},$$

where  $\eta_L$ ,  $\eta_s$ ,  $\dot{\gamma}$ ,  $n$  and  $z$  are respectively the solution viscosity after degradation, the solvent viscosity, the shear rate, the number of moles of polymer per unit volume of solution, and the mean extension of the polymer molecule normal to flow. Calculated values of the degrading force for PS in good and poor solvents were  $3.5 \times 10^{-6}$  dyn and  $4 \times 10^{-7}$  dyn, respectively. The value for DNA in phosphate buffer was  $2.7 \times 10^{-5}$  dyn<sup>10</sup>. Similar calculations of critical stress values have been made for the case of a high-speed stirrer<sup>13</sup>.

In another publication<sup>40</sup>, the force was expressed by the relation

$$f_c = \frac{(\eta_L - \eta_s)\tau M_L}{\eta_L N_0 z n} \quad (N_0 \text{ is Avogadro's number})$$

and a plot of  $\frac{\tau}{n\eta_L} (\eta_L - \eta_s)$  against  $\frac{1}{M_L}$  gave a straight line through the origin. Hence for every molecular weight, there exists a critical value of the parameter  $\frac{\tau}{n\eta_L} (\eta_L - \eta_s)$  below which no degradation occurs and this parameter was used as a criterion for degradation.

## 5 ENERGETICS

The work of degradation was calculated for PIB in mineral oil<sup>105</sup>.

Bestul, in a series of experiments with a capillary, has used values of viscosity-average molecular weights to compute rate constants for the scission reaction<sup>33,35,36,38,39</sup>. He then found the following relationship between the rate constant,  $k$ , and the rate of energy application per unit volume of solution,  $\tau\dot{\gamma}$ , the latter being estimated from the pressure drop across the capillary:



$$k = C \exp \left[ - \frac{E}{a\tau\dot{\gamma}} \right] .$$

The coefficient  $a$  is a factor such that  $a\tau\dot{\gamma}$  is some function of the average amount of mechanical energy temporarily stored in the chemical bonds of the system;  $E$  is the activation energy required for bond rupture and  $C$  is a constant. In the temperature range  $60^{\circ}$ – $80^{\circ}\text{C}$ , the rate constant decreased with increasing temperature, whereas at lower temperatures there was no variation of the rate constant with temperature. The energy input requirements for degradation showed an increase with increasing temperature. Thus at a shear rate of  $5 \times 10^4 \text{ s}^{-1}$ , the degradation energy was  $3.6 \times 10^5 \text{ kcal/mol}$  at  $60^{\circ}\text{C}$  and  $4.67 \times 10^5 \text{ kcal/mol}$  at  $80^{\circ}\text{C}$ . The variation of the rate constant with the rate of shear-energy application decreased with increasing initial molecular weight but did not vary with concentration, in agreement with a first-order rate law.

Other workers have also identified the energy discharged per unit volume as a parameter which determines the amount of degradation<sup>62,83</sup>.

A concentric cylinder viscometer specially fitted with a flow-through attachment has been used to estimate the efficiency of degradation<sup>67</sup>. The results indicated the inefficiency of bond rupture, with over a million times the energy being required to produce a mole of broken bonds as compared with the activation energy of carbon-carbon bond rupture ( $50$ – $80 \text{ kcal/mol}$ ). Again, the efficiency decreased with increasing temperature.

A very crude comparison of the results obtained from the capillary and rotational-viscometer experiments may be made as follows:

(a) For 10% PIB w/w of  $\bar{M}_v 9.1 \times 10^5$  in cetane sheared in a capillary at a shear rate of  $66000 \text{ s}^{-1}$  at  $40^{\circ}\text{C}$ , the degradation energy per mole of ruptured bonds was  $3 \times 10^5 \text{ kcal}$ <sup>39</sup>.

(b) For 9.7% w/v of PIB of  $\bar{M}_v 8 \times 10^5$  in trichlorobenzene sheared in a rotational viscometer at a shear rate of  $172\,000 \text{ s}^{-1}$  at  $40^{\circ}\text{C}$ , the estimated degradation energy per mole of ruptured bonds was of the order of  $5 \times 10^5 \text{ kcal}$ , assuming an average flow rate of  $0.075 \text{ cm}^3$  per minute and a degradation time of  $2 \text{ s}$ <sup>67</sup>. This means that, despite the different conditions used in the two cases, the estimated efficiencies are in the same order of magnitude.

## 6 MECHANISMS OF DEGRADATION

Mechanical degradation can be regarded as a chemical-scission reaction whose activation energy is supplied mechanically. However, the average mechanical

energy supplied to a volume occupied by two covalently-bound methylene groups is much smaller than the activation energy. This was demonstrated<sup>33</sup> for capillary degradation where the required activation energy could only be developed in a volume of  $3 \times 10^{-19} \text{ cm}^3$ , whereas the covalent-bond volume was  $10^{-23} \text{ cm}^3$ . Since the volume occupied by the high polymer molecule in solution was at least  $3 \times 10^{-18} \text{ cm}^3$ , a bond only breaks if the energy developed in one tenth of this volume can be concentrated into a single bond as temporarily stored potential energy. It was estimated<sup>39</sup> that about 4000 bonds were involved in concentrating energy into the ruptured bond, both as potential energy and as configurational entropy.

When polymer molecules in solution are sheared, their configuration becomes extended in the direction of flow<sup>62</sup>. The limiting molecular weight was regarded as the chain length short enough to adjust to the stress by moving with respect to its sheath of solvent molecules, than by breaking bonds in the polymer backbone<sup>12</sup>. The stretching forces tending to cause rupture reach a maximum for the central chemical bond and, for a given shear stress, they increase with the square of the molecular length<sup>53,102</sup>. Larger molecules are therefore ruptured preferentially. These stretching forces have been calculated for molecules sheared near the leading edge of stirrer blades<sup>13</sup> and other types of degrader<sup>10</sup>. The force distribution along the polymer molecule was thought to be ideally parabolic, with the maximum in the centre. However, because of the variation in stress along a polymer molecule due to inhomogeneous shear fields around the stirrer and capillary, the maximum force could be shifted nearer to one end of the molecule, resulting in a molecular weight distribution broader than the ideal one. Polymer molecules, on entering an area of turbulent flow, can also be caught in eddies moving in different directions<sup>28</sup>.

One aspect of the mechanism of polymer degradation which remains unclear is the role which entanglements play in concentrating mechanical energy. The polymer concentrations used have varied from a few parts per million, where it may be assumed that polymer molecules are virtually isolated one from another, to highly concentrated solutions where the molecules are highly entangled. Since degradation can occur even at the low concentrations, it is clear that entanglement is not a necessary condition for the occurrence of degradation. This was shown by Minoura and coworkers<sup>22,23,25,26,46</sup> who found that the degradation was unaffected by a change in concentration in the range 1-5%. This would not be expected if entanglement were involved as an increase in concentration should give more entanglements thereby leading to more degradation. In this case,

degradation was regarded as occurring by polymer-solvent interactions, not by polymer-polymer interactions. In a shear field, some segments of a polymer chain which is somewhat expanded move at high speed whereas other segments move at lower speeds, producing a tensile force on the polymer chain. Polymer molecules were ruptured to a constant hydrodynamic volume,  $[\eta]M$ , regardless of solvent ( $[\eta]$  is the intrinsic viscosity of polymer of molecular weight  $M$ ).

Bueche has put forward a theory of degradation which involves the participation of entanglements<sup>106</sup>. As a molecule rotates under shear it alternately stretches and contracts in a sinusoidal oscillation. At very high shear rates, the molecule rotates so fast that the chain is not able to distort much in response to the applied shear. This would normally give little degradation. However, entangled molecules must disentangle from one another for flow to occur. Even for low shear rates, segments must move swiftly to release entanglements without developing very large forces. Under high shear, such large forces are built up as a result of entanglements and this leads to rupture. Again, the maximum force is built up at chain centres and in the ideal case, where scission always occurs at the centre points, the limiting molecular weight distribution would span molecular weights from  $M_L/2$  to  $M_L$ : a chain of molecular weight slightly larger than  $M_L$  will still have a chance of breaking, giving a chain of molecular weight slightly larger than  $M_L/2$ .

The results of other workers appear to be consistent with this theory<sup>41, 61, 76</sup>. However, the observation of the presence of very low molecular weight polymers after degradation at high shear stresses could only be explained by saying that the chains ruptured before they had time to extend to their equilibrium conformations<sup>65, 76</sup>.

According to Johnson<sup>63, 65, 67</sup>, degradation occurred at entanglement points on a network of polymer chains rather than *via* individual molecules.

An increase in initial molecular weight and a decrease in temperature both led to an increased efficiency in the process of temporarily concentrating mechanical energy by means of entanglements<sup>35, 36</sup>.

There is good evidence that the chemical mechanism of degradation involves the formation of free radicals. Thus PEO radicals formed by high-speed stirring under nitrogen were used to form block copolymers with other monomers and the rate of polymerisation was proportional to the square root of the shear rate, suggesting a radical mechanism<sup>20</sup>. In another experiment<sup>12</sup>, radical production was



estimated by the addition of radio-iodine. During degradations in air, radicals formed by shearing will normally be prevented from recombining by the action of oxygen molecules as fast and efficient radical acceptors. This is perhaps why many investigators found that the addition of chemicals, as radical acceptors, did not greatly affect the amount of degradation. Chemical additives used included the coloured radical diphenyl picryl hydrazyl<sup>13,72</sup>, thio- $\beta$ -naphthol<sup>3</sup>, and phenyl- $\beta$ -naphthylamine<sup>26,34</sup>.

## 7 CONCLUSIONS

The papers quoted in this review span the period 1930-1975 and they vary greatly in the depth in which the subject of mechanical degradation has been examined. In some, a detailed quantitative examination of the results is given, whilst in others only qualitative statements are made. In the years before the development of gel permeation chromatography, no accurate data on molecular weight distributions were available and so the course of the degradation was more difficult to follow. For the purpose of summarising the results it is, therefore, reasonable to place more emphasis on the more recent detailed studies than on some of the earlier publications whose findings conflict at times with later work. Particular note has been taken of the series of reports by Bestul<sup>32-39</sup>, Harrington<sup>10,13,59</sup>, Johnson<sup>62-68</sup>, Minoura<sup>20-26</sup> and Kadim<sup>40</sup> in drawing up the following list of statements about mechanical degradation which are supported by the majority of the evidence.

- (a) Mechanical shearing of polymers in solution can result in cleavage of the polymer backbone producing free radicals and a reduction in molecular weight.
- (b) For given shear conditions, the rate of reduction in molecular weight is rapid at first but slows down with increasing time or number of passes until a limiting molecular weight  $M_L$  is reached, characteristic of the shear stress.
- (c) The rate of bond breakage is proportional to the number of cleavable bonds.
- (d) The extent of degradation for a given polymer is determined more by the shear stress obtained than by the rate of shear. Thus, a higher shear stress degrades the polymer at a higher initial rate down to a lower limiting molecular weight.



(e) At a fixed shear rate, the extent of degradation decreases with increasing temperature, but at a fixed shear stress, temperature variation has little or no effect on the degradation.

(f) For fixed shear conditions, the initial rate of degradation increases with increasing initial molecular weight but a common limiting molecular weight is eventually obtained.

(g) For polymers with an initially wide distribution of molecular weight, a narrowing of the distribution may often be obtained after degradation.

(h) Polymers degrade to a greater extent in the so-called 'poor' solvents than in 'good' solvents, other factors being the same.

(i) Polymer degradation is affected by changes in concentration of the polymer but in a manner which is different for different polymers and different ranges of concentration.

(j) For mechanical degradation to occur, the mechanical energy must be concentrated into the bond to be broken, either by an entanglement mechanism or by the development of large forces on a molecule of polymer when different sections of the chain move at different speeds in response to the applied shear.

(k) The efficiency of the process of temporarily concentrating mechanical energy into bonds is very low but increases with decreasing temperature or increasing initial molecular weight. Thus the lower the temperature, the less the energy input to achieve a given amount of degradation.

Table 1  
EXAMPLES OF SHEAR CONDITIONS

Device	Polymer	Concn. %	Solvent	T°C	$\dot{\gamma}^*$	$\tau^*$	$M_0(\times 10^{-5})^*$	$M(\times 10^{-5})^*$	Ref.
Agitation	PIB	Various	Toluene etc.	30			120	30	2
Stirrer	PS, DNA	0.01-0.12	Various	25			107	0.64	10
Stirrer	PIB	3-20	Cetane	40	$1 \times 10^5$		17.4	12.4	11
Stirrer	PS, PIB	1-4	Various	5-40			17	2.8	12
Stirrer	PS, DNA		Various	25			30	2	13
Stirrer	PEO	2-5	Various	25-40			17	1.3	21
Stirrer	PEO, PMMA	1-4	Benzene	20			6.4	1.33	22
Stirrer	PS, PMMA, PIB	2	Various	30			9.3	1.46	25
Stirrer	PS, PMMA	0.04-2	Various	30			16	1.51	26
Capillary	PIB	5-15	$C_6H_4Cl_2$	40	$6.6 \times 10^4$		20	16	32
Capillary	PIB	5-15	$C_6H_4Cl_2$	38	$6.5 \times 10^4$		23	5	33
Capillary	PIB	5-20	Cetane	20-80	$6.6 \times 10^4$		25.2	11.3	34
Capillary	PIB	10	Cetane	60, 80	$1.34 \times 10^5$		17.4	13.7	35
Capillary	PIB	5-15	Cetane	30-50	$6.6 \times 10^4$		25.2	8.6	36
Capillary	PIB	10	Cetane	40	$6.6 \times 10^4$		17.4	11.5	37
Capillary	PIB	10	Cetane	40	$5.0 \times 10^4$		17.4	12.4	38
Capillary	PIB	5-20	Cetane	20-80	$6.6 \times 10^4$		25.2	7.4	39
Capillary	PS	0.04-0.06	Various	25	$\sim 10^6$		107	30	10
Capillary	PIB	0.26-1	Decalin	30, 60		$1.5 \times 10^4$	64	7.5	40
Capillary	PAA	0.004	Water	25			70.4	3	41
Atomiser	DNA		Water	25			33	12	60
Atomiser	DNA	0.03-0.08	Water	0-60	$\sim 10^5$		35	10	61
Viscometer	PIB	Various	Decalin	30	$9.6 \times 10^4$	$1.7 \times 10^4$	22	20	2
Viscometer	PIB	10	Cetane	25-80	$3.4 \times 10^5$	$1.3 \times 10^5$	22.4	$\sim 4$	62
Viscometer	PIB	4, 10	Cetane	60	$3.3 \times 10^5$	$\sim 10^5$	8	2.7	63
Viscometer	PIB	10	Cetane	20-60	$7 \times 10^5$	$10^6$	8	1.5	65
Viscometer	PIB	10	Cetane	20-60	$7.15 \times 10^5$	$1.67 \times 10^5$	8	2	67
Viscometer	PIB	2	Cyclohexane	30	$10^5$		22	20.6	72
Viscometer	PMMA	0.56-1.7	Various	23	3420	3760	38	21.5	73
Viscometer	PAA	0.2, 0.7	Water	25, 40	$1.15 \times 10^5$	$5.7 \times 10^4$	22	19	76
Pipe	Various	0.004	Water	20	$4 \times 10^5$	4200	70	10	83
Pipe	PIB	0.015-0.06	Kerosine		$5.5 \times 10^4$		50	4	93
Disc	PIB	0.1-0.25	Kerosine	24-31	$10^5$		20	4.85	28
Piston	PS	0.06		25	$4.4 \times 10^6$		107	16	10
Sinter	PS	0.06	Toluene	25			107	5.4	10

\* Shear rates and shear stresses are the maximum values quoted and the units are respectively  $s^{-1}$  and  $\text{dyn/cm}^2$ ; molecular weights,  $M$ , for degraded polymers are the minimum quoted values.

SYMBOLS

C	constant
E	activation energy required for bond rupture
M	molecular weight of polymer at a particular stage of degradation
$M_c$	highest molecular weight present after shear
$M_L$	limiting molecular weight of the polymer
$M_0$	molecular weight of the undegraded polymer
$N_0$	Avogadro's number
PAA	polyacrylamide
PEO	poly(ethylene oxide)
PIB	polyisobutylene
PMA	polymethacrylic acid
PMMA	poly(methyl methacrylate)
PS	polystyrene
DNA	deoxyribonucleic acid
k	rate constant of scission
m	molecular weight of monomer
$n_M$	number of moles of polymer of molecular weight M per $\text{cm}^3$ of solution
$\frac{dn_M}{dt}$	rate of scission of molecules of molecular weight M
w	weight of polymer per $\text{cm}^3$ of solution
z	mean extension of the polymer molecule normal to flow
$f_c$	critical force required to cause chain scission
$\dot{\gamma}$	shear rate (units: $\text{s}^{-1}$ )
$\eta_s$	viscosity of the solvent
$\eta_L$	solution viscosity at the limit of degradation
$[\eta]$	intrinsic viscosity

REFERENCES

- | <u>No.</u> | <u>Author</u>  | <u>Title, etc.</u>   |
|------------|--|--|
| 1          | A. Casale<br>J.F. Johnson<br>R.S. Porter                   | The mechanochemistry of high polymers.<br><i>Rubber Chem. Technol.</i> , <u>44</u> , 534 (1971)  |
| 2          | E.W. Merrill<br>H.S. Mickley<br>A. Ram                     | Degradation of polymers in solution induced by turbulence and droplet formation.<br><i>J. Polym. Sci.</i> , <u>62</u> , S109 (1962)  |
| 3          | R.J. Ceresa<br>W.F. Watson                                 | Mastication of rubber. VII Mechanical degradation of polymers during mastication.<br><i>J. Appl. Polym. Sci.</i> , <u>1</u> , 101 (1959)   |
| 4          | V.P. Alachev<br>T.V. Tsaranova<br>E.V. Zobov               | Mechanical degradation of poly(methyl methacrylate) in solutions by the action of a vibratory mill.<br><i>Chem. Abs.</i> , <u>71</u> , 39679u (1969)                                   |
| 5          | A.F. Preuss<br>R.L. Stambaugh                              | Laboratory methods for predicting viscosity loss of polymer thickened hydraulic fluids.<br>SAE paper 680438 for meeting 20-24 May, 1968  |
| 6          | T.D. Foster<br>E.R. Mueller                                | Effect of polymer structure on shear stability of polymer thickened power transfer fluids.<br>ASTM Special Tech. Publ. 382, pp.14-32 (1965)  |
| 7          | V. Hopkins<br>D.R. Wilson                                  | High temperature shear stability of potential hydraulic fluids.<br>Presented at the 1963 USAF Aerospace Fluids and Lubricants Conf., Session V-A, San Antonio, Texas, 16-19 April 1963 |
| 8          | C.D. Green<br>H.C. Hershey<br>G.K. Patterson<br>J.L. Zakin | Effect of degradation by pumping on normal stresses in polyisobutylene solutions.<br><i>Trans. Soc. Rheol.</i> , <u>10</u> , 489 (1966)  |
| 9          | P. Alexander<br>M. Fox                                     | The role of free radicals in the degradation of high polymers by ultrasonics and by high-speed stirring.<br><i>J. Polym. Sci.</i> , <u>12</u> , 533 (1954)                             |
| 10         | R.E. Harrington<br>B.H. Zimm                               | Degradation of polymers by controlled hydrodynamic shear.<br><i>J. Phys. Chem.</i> , <u>69</u> , 161 (1965)  |



REFERENCES (continued)

- | <u>No.</u> | <u>Author</u>                                       | <u>Title, etc.</u>  |
|------------|---|---|
| 11         | A. Bendich<br>H.S. Rosenkranz                       | Physicochemical effects of high-speed mixing on deoxyribonucleic acid.<br><i>J. Amer. Chem. Soc.</i> , <u>82</u> , 3198 (1960)  |
| 12         | W.R. Johnson<br>C.C. Price                          | Shear degradation of vinyl polymers in dilute solution by high-speed stirring.<br><i>J. Polym. Sci.</i> , <u>45</u> , 217 (1960)  |
| 13         | R.E. Harrington                                     | Degradation of polymers in high speed rotary homogenisers: a hydrodynamic interpretation.<br><i>J. Polym. Sci.</i> , Part A-1, <u>4</u> , 489 (1966)                      |
| 14         | G.S. Banker<br>D.R. Powell<br>J. Swarbrick          | Effects of shear processing and thermal exposure on the viscosity-stability of polymer solutions.<br><i>Chem. Abs.</i> , <u>65</u> , 9157b (1966)                         |
| 15         | J.W. Breitenbach<br>J.K. Rigler<br>B.A. Wolf        | Degradation of polystyrene in cyclohexane solution at a low shearing rate.<br><i>Makromol. Chem.</i> , <u>164</u> , 353 (1973)  |
| 16         | H. Fujiwara<br>K. Goto                              | Mechano-chemical polymerisation of vinyl acetate.<br><i>J. Polym. Sci.</i> , Part B, <u>1</u> , 505 (1963)  |
| 17         | H. Fujiwara<br>K. Goto                              | Mechanical degradation of poly(vinyl acetate) in solution induced by vigorous stirring.<br><i>Chem. Abs.</i> , <u>62</u> , 10536g (1965)                                  |
| 18         | H. Fujiwara<br>K. Goto                              | Reaction rate for mechanical degradation of polymers.<br><i>Kobunshi Kagaku</i> , <u>23</u> , 827 (1966)<br><i>Chem. Abs.</i> , <u>67</u> , 22375m (1967)                 |
| 19         | H. Fujiwara<br>K. Goto                              | Mechanical degradation of vinyl polymers in solutions.<br><i>Chem. Abs.</i> , <u>70</u> , 38340u (1969)   |
| 20         | T. Kasuya<br>S. Kawamura<br>Y. Minoura<br>A. Nakano | Block copolymerisation of methyl methacrylate with poly(ethylene oxide) radicals formed by high-speed stirring.<br><i>J. Polym. Sci.</i> , Part A-1, <u>5</u> , 43 (1967) |
| 21         | T. Kasuya<br>S. Kawamura<br>Y. Minoura<br>A. Nakano | Degradation of poly(ethylene oxide) by high-speed stirring.<br><i>J. Polym. Sci.</i> , Part A-2, <u>5</u> , 125 (1967)  |

REFERENCES (continued)

- | <u>No.</u> | <u>Author</u>                | <u>Title, etc.</u>   |
|------------|------------------------------|--|
| 22         | Y. Minoura<br>A. Nakano      | Degradation of polymers by high-speed stirring.<br><i>J. Appl. Polym. Sci.</i> , <u>15</u> , 927 (1971)  |
| 23         | Y. Minoura<br>A. Nakano      | Chemical reactions of polymers studied using mechanical force. III Mechanical degradation of polymers with high-speed stirring.<br><i>Chem. Abs.</i> , <u>74</u> , 142736w (1971)    |
| 24         | Y. Minoura<br>A. Nakano      | Chemical reactions of polymers under mechanical force. IV Effect of solvent on the degradation of polymers by high-speed stirring.<br><i>Chem. Abs.</i> , <u>75</u> , 152268e (1971) |
| 25         | Y. Minoura<br>A. Nakano      | Effect of solvents on the degradation of polymers by high-speed stirring.<br><i>J. Appl. Polym. Sci.</i> , <u>16</u> , 627 (1972)  |
| 26         | Y. Minoura<br>A. Nakano      | Effects of solvent and concentration on scission of polymers with high-speed stirring.<br><i>J. Appl. Polym. Sci.</i> , <u>19</u> , 2119 (1975)                                      |
| 27         | G.E. Gadd                    | Turbulence damping and drag reduction produced by certain additives in water.<br><i>Nature</i> , <u>206</u> , 463 (1965)   |
| 28         | F. Rodriguez<br>C.C. Winding | Mechanical degradation of polyisobutylene solutions.<br><i>Ind. Eng. Chem.</i> , <u>51</u> , 1281 (1959)   |
| 29         | H. Staudinger                | Mechanical break-up of polymer solutions.<br><i>Chem. Ber.</i> , <u>63</u> , 3152 (1930)   |
| 30         | W. Heurer<br>H. Staudinger   | Highly polymerised compounds. XCIII The breaking up of the molecular fibres of the polystyrenes.<br><i>Chem. Ber.</i> , <u>67</u> , 1159 (1934)                                      |
| 31         | E. Dreher<br>H. Staudinger   | Highly polymerised compounds. CXXXVIII The rupture of the thread-like molecules of cellulose upon heating.<br><i>Chem. Ber.</i> , <u>69</u> , 1091 (1936)                            |

REFERENCES (continued)

- | <u>No.</u> | <u>Author</u>   | <u>Title, etc.</u>   |
|------------|---|--|
| 32         | H.V. Belcher<br>A.B. Bestul   | Degradation of different molecular weight polyisobutylenes on shearing in solution.<br><i>Phys. Rev.</i> , <u>79</u> , 223 (1950)  |
| 33         | H.V. Belcher<br>A.B. Bestul   | Degradation of polyisobutylenes on shearing in solution.<br><i>J. Appl. Phys.</i> , <u>24</u> , 1011 (1953)  |
| 34         | A.B. Bestul   | Composition of apparent shearing forces during shear degradation of polymers.<br><i>J. Appl. Phys.</i> , <u>25</u> , 1069 (1954)   |
| 35         | A.B. Bestul<br>P. Goodman   | Temperature dependence of mechanical shear degradation.<br><i>J. Polym. Sci.</i> , <u>18</u> , 235 (1955)  |
| 36         | A.B. Bestul   | Kinetics of capillary shear degradation in concentrated polymer solutions.<br><i>J. Chem. Phys.</i> , <u>24</u> , 1196 (1956)  |
| 37         | A.B. Bestul   | Evidence for mechanical shear degradation of high polymers.<br><i>J. Phys. Chem.</i> , <u>61</u> , 418 (1957)  |
| 38         | P. Goodman  | Dependence of mechanical shear degradation of polymers in solution on rate of energy application and on concentration.<br><i>J. Polym. Sci.</i> , <u>25</u> , 325 (1957) |
| 39         | A.B. Bestul   | Energy requirements of mechanical shear degradation in concentrated polymer solutions.<br><i>J. Chem. Phys.</i> , <u>32</u> , 350 (1960)                                 |
| 40         | A. Kadim<br>A. Ram  | Shear degradation of polymer solutions.<br><i>J. Appl. Polym. Sci.</i> , <u>14</u> , 2145 (1970)   |
| 41         | P. Kumar<br>J.H.T. Wade   | Electron microscope studies of polymer degradation.<br><i>J. Hydronautics</i> , <u>6</u> , 40 (1972)   |
| 42         | J.D. Culter<br>K.G. Mayhan<br>G.K. Patterson<br>A.A. Sarmasti<br>J.L. Zakin | Entrance effects on capillary degradation of dilute polystyrene solutions.<br><i>J. Appl. Polym. Sci.</i> , <u>16</u> , 3381 (1972)                                      |

REFERENCES (continued)

<u>No.</u>	<u>Author</u>	<u>Title, etc.</u>
43	D.E. Moore A.G. Parts	Mechanical degradation of polystyrene in solution. <i>Polymer</i> , <u>9</u> , 52 (1968)
44	T. Fukutomi T. Kakurai T. Noguchi Y.M. Won	Mechanical degradation of polymers in dilute solutions. Influence of the temperature on scission. <i>Chem. Abs.</i> , <u>76</u> , 15058t (1972)
45	Y.M. Won	Mechanical degradation of polymers in dilute solution. II Influence of mixed solvents. <i>Chem. Abs.</i> , <u>77</u> , 35175c (1972)
46	Y.M. Won	Mechanical degradation of polymers in dilute solution. III Influence of mixed solvents. <i>Chem. Abs.</i> , <u>79</u> , 53963d (1973)
47	J.K. Lund H.A. Pohl	Chain rupture by shear in molten polymer. <i>Soc. Petroleum Eng. J.</i> , <u>15</u> , 390 (1959)
48	P.F. Davison D. Levinthal	Shear degradation and the molecular weight of deoxyribonucleic acid. <i>J. Mol. Biol.</i> , <u>3</u> , 674 (1961) <i>Chem. Abs.</i> , <u>56</u> , 2698g and 10539a (1962)
49	H. Grohn F. Krause	Mechanochemical degradation of high polymers in solution by capillary shear. I Dependence of degrada- tion on mechanical conditions and II Concentration dependence of degradation. <i>Chem. Abs.</i> , <u>61</u> , 8432g (1964)
50	V.E. Dreval M.S. Lutsky A.A. Tager	Rheological behaviour of concentrated polystyrene solutions in good and poor solvents. <i>J. Polym. Sci.</i> , Part C, <u>23</u> , 181 (1968)
51	K. Arai T. Komatsu T. Nakagawa K. Nakamura	Mechanical shear degradation of polystyrene in solution. <i>Chem. Abs.</i> , <u>70</u> , 29458m (1969)



REFERENCES (continued)

<u>No.</u>	<u>Author</u>	<u>Title, etc.</u>
52	W.J. Morris R. Schnurmann	A jet viscometer with variable rate of shear. <i>Rev. Sci. Instr.</i> , <u>17</u> , 17 (1946)
53	W.J. Morris R. Schnurmann	Mechanical degradation of large molecules. <i>Nature</i> , <u>160</u> , 674 (1947)
54	H. Kinoshita R. Kiyama	Degradation of the polyethylene molecule by a high-pressure jet. <i>Chem. Abs.</i> , <u>47</u> , 5765a (1953)
55	L.G. Wood	The change of viscosity of oils containing high polymers when subjected to high rates of shear. <i>Brit. J. Appl. Phys.</i> , 202 (1950)
56	A.E. Jemmett K. Mackenzie	Polymer shear stability. <i>Wear</i> , <u>17</u> , 389 (1971)
57	E. Abrysowska L. Guminska W. Pawlowski	Mechanical stability of high polymeric lubricant additives. <i>Schmierstoffe u. Schmierungstechn.</i> , <u>9</u> , 48 (1966) <i>Chem. Abs.</i> , <u>68</u> , 61269v (1968)
58	P.A. Bylym N.N. Kruglitskii	Mechanochemical degradation of polyacrylamide during its mixing with water. <i>Chem. Abs.</i> , <u>79</u> , 32531w (1973)
59	R.E. Harrington B.H. Zimm	Anomalous plugging of sintered glass filters by high molecular weight polymers. <i>J. Polym. Sci.</i> , Part A-2, <u>6</u> , 294 (1968)
60	L.F. Cavalieri	Paucidisperse deoxyribonucleic acid and its use in the study of genetic determinants. <i>J. Amer. Chem. Soc.</i> , <u>79</u> , 5319 (1957)
61	L.F. Cavalieri B.H. Rosenberg	Shear degradation of deoxyribonucleic acid. <i>J. Amer. Chem. Soc.</i> , <u>81</u> , 5136 (1959)
62	J.F. Johnson R.S. Porter	Laminar flow degradation of polyisobutene. <i>J. Phys. Chem.</i> , <u>63</u> , 202 (1959)
63	J.F. Johnson R.S. Porter	Polyisobutene degradation in laminar flow: composition and shear variables. <i>J. Appl. Phys.</i> , <u>35</u> , 3149 (1964)

REFERENCES (continued)

<u>No.</u>	<u>Author</u>	<u>Title, etc.</u>
64	J.F. Johnson R.F. Klaver R.S. Porter	Recording high shear viscometer for measurement at shear rates near $10^6 \text{ s}^{-1}$ . <i>Rev. Sci. Instr.</i> , <u>36</u> , 1846 (1965)
65	M.J.R. Cantow J.F. Johnson R.S. Porter	Polyisobutene degradation in laminar flow: the effect on molecular weight distribution. <i>J. Polym. Sci.</i> , Part C, <u>16</u> , 1 (1967)
66	M.J.R. Cantow J.F. Johnson R.S. Porter	A comparison of molecular weight distributions for polyisobutenes as determined from gel permeation and gradient elution chromatographic fractionations. <i>J. Polym. Sci.</i> , Part C, <u>16</u> , 13 (1967)
67	M.J.R. Cantow J.F. Johnson R.S. Porter	Polymer degradation. VI Distribution changes on polyisobutene degradation in laminar flow. <i>Polymer</i> , <u>8</u> , 87 (1967)
68	J.F. Johnson W.J. MacKnight R.S. Porter	Viscous and elastic behaviour attributed to polymer entanglements. <i>Rubber Chem. Technol.</i> , <u>41</u> , 1 (1968)
69	N.I. Kaverina	Mechanical degradation of polyisobutylene in mineral oil solutions. <i>Chem. Abs.</i> , <u>51</u> , 4687i (1957) English translation: <i>J. Appl. Chem. USSR</i> , <u>29</u> , 1565 (1956)
70	N.I. Kaverina E.G. Semenido	Change in molecular weight and fractional composition of polyisobutylene in the process of degradation in mineral oil solution. <i>J. Appl. Chem. USSR</i> , <u>29</u> , 1993 (1956)
71	K.I. Klimov P.P. Zarundii	Mechanical destruction of solutions of polyisobutylenes in mineral oils. <i>Khim. Tekhnol. Topliv Masel</i> , <u>4</u> , 37 (1959) <i>Chem. Abs.</i> , <u>53</u> , 8694f (1959)
72	E.W. Merrill H.S. Mickley A. Ram	Effect of shear on intrinsic viscosity of a whole polyisobutylene in cyclohexane. <i>J. Polym. Sci.</i> , <u>51</u> , S43 (1961)

REFERENCES (continued)

<u>No.</u>	<u>Author</u>	<u>Title, etc.</u>
73	M. Bohdanecky O. Quadrat	Negative thixotropy of poly(methyl methacrylate) solutions in $\theta$ -solvents. <i>J. Polym. Sci.</i> , Part A-2, <u>5</u> , 1309 (1967)
74	Y. Go Y. Kondo T. Okamura E. Yambe	Mechanical denaturation of high polymer solutions. <i>Chem. Abs.</i> , <u>69</u> , 97283e (1968)
75	A. Deluzarche A. Maillard	Shearing degradation of high polymers dissolved in mineral oils. <i>Chem. Abs.</i> , <u>73</u> , 47228c (1970)
76	A.H. Abdel-Alim A.E. Hamielec	Shear degradation of water-soluble polymers. I Degradation of polyacrylamide in a high-shear couette viscometer. <i>J. Appl. Polym. Sci.</i> , <u>17</u> , 3769 (1973)
77	A.G. Fabula J.W. Hoyt	The effect of additives on fluid friction. US Naval Ordnance Test Station, China Lake, Calif. NAVWEPS - 8636 (1964)
78	J.W. Hoyt	Friction reduction as an estimator of molecular weight. <i>J. Polym. Sci.</i> , Part B, <u>4</u> , 713 (1966)
79	C. Brennen G.E. Gadd	Reduction of turbulent drag in liquids. <i>Nature</i> , <u>215</u> , 1368 (1970)
80	F.H. Abernathy R.W. Paterson	Turbulent flow drag reduction and degradation with dilute polymer solutions. <i>J. Fluid. Mech.</i> , <u>43</u> , 689 (1970)
81	D.A. White	Preliminary experiments on polymer degradation in a turbulent shear field. <i>Chem. Eng. Sci.</i> , <u>25</u> , 1255 (1970)
82	D.H. Fisher F. Rodriguez	Degradation of drag-reducing polymers. <i>J. Appl. Polym. Sci.</i> , <u>15</u> , 2975 (1971)

REFERENCES (continued)

- | <u>No.</u> | <u>Author</u>                                      | <u>Title, etc.</u>  |
|------------|--|---|
| 83         | P.R. Kenis   | Turbulent flow friction reduction effectiveness and hydrodynamic degradation of polysaccharides and synthetic polymers.<br><i>J. Appl. Polym. Sci.</i> , <u>15</u> , 607 (1971) |
| 84         | B.J.S. Barnard<br>R.H.J. Sellin                    | Degradation of dilute solutions of drag-reducing polymer.<br><i>Nature (London) Phys. Sci.</i> , <u>236</u> , 12 (1972)   |
| 85         | N.A. Gason-Zade<br>R.S. Gurbanov<br>K.A. Tagi-Zade | Effect of different factors on the degradation of aqueous solutions of polymers.<br><i>Chem. Abs.</i> , <u>77</u> , 62408n (1972)   |
| 86         | I.M. Felsen<br>T.G. Smith                          | Turbulent flow drag reduction by dilute poly(ethylene oxide) solutions in capillary tubes.<br><i>Chem. Abs.</i> , <u>79</u> , 66938z (1973)                                     |
| 87         | P.K. Amar<br>P.I. Gold<br>B. Swaidan               | Friction reduction degradation in dilute poly(ethylene oxide) solutions.<br><i>J. Appl. Polym. Sci.</i> , <u>17</u> , 333 (1973)  |
| 88         | B.C. Ramakrishnan<br>F. Rodriguez                  | Drag reduction in non-aqueous liquids.<br><i>Chem. Abs.</i> , <u>79</u> , 66937y (1973)   |
| 89         | S.M. Kumor<br>N.D. Sylvester                       | Degradation of dilute polymer solutions in turbulent tube flow.<br><i>Chem. Abs.</i> , <u>79</u> , 53944y (1973)  |
| 90         | R.C. Little<br>R.Y. Ting                           | Characterisation of drag reduction and degradation effects in the turbulent pipe flow of dilute polymer solutions.<br><i>J. Appl. Polym. Sci.</i> , <u>17</u> , 3345 (1973)     |
| 91         | H.D. Ellis   | Effects of shear treatment on drag-reducing polymer solutions and fibre suspensions.<br><i>Nature</i> , <u>226</u> , 352 (1970)   |
| 92         | A.T. Ellis<br>R.H. Nadolink<br>R.Y. Ting           | Some storage and shear history effects on polymeric friction reduction.<br><i>J. Hydronautics</i> , <u>6</u> , 66 (1972)  |



REFERENCES (continued)

<u>No.</u>	<u>Author</u>	<u>Title, etc.</u>
93	C. Elata E. Finkelstein A. Ram	Reduction of friction in oil pipelines by polymer additives. <i>Ind. Eng. Chem., Process Design Development</i> , <u>6</u> , 309 (1967)
94	A. Ram A. Tamir	Structural turbulence in polymer solutions. <i>J. Appl. Polym. Sci.</i> , <u>8</u> , 2751 (1964)
95	E. Jenckel F. Sonntag	Mechanical degradation of chain molecules in solution by collisions of suspended solids. <i>Chem. Abs.</i> , <u>48</u> , 6195c (1954)
96	V.P. Avtaikin T. Dmitrieva G.A. Gorokhovskii	Factors determining the mechanical degradation of polymers in solutions. <i>Chem. Abs.</i> , <u>81</u> , 136829g (1974)
97	L.J. Fetters E.L. Slagowski	Upper molecular weight limit for the characterisation of polystyrene in gel permeation chromatography. <i>Macromolecules</i> , <u>7</u> , 394 (1974)
98	P.F. Davison	Effect of hydrodynamic shear on the LNA from bacteriophages. <i>Chem. Abs.</i> , <u>54</u> , 4712b (1960)
99	H.H.G. Jellinek G. White	The degradation of long chain molecules by ultrasonic waves. I Theoretical. <i>J. Polym. Sci.</i> , <u>6</u> , 745 (1951)
100	P.E.M. Allen G.W. Hastings D.W. Ovenall	The degradation of polymer molecules in solution under the influence of ultrasonic waves. I Kinetic analysis. <i>J. Polym. Sci.</i> , <u>33</u> , 207 (1958)
101	P. Borgstrom H.A. Pohl W.A. Zisman	Viscosity breakdown of oils. <i>Naval Research Lab. Report</i> , P2075 (1943)
102	Y. Frenkel	Orientation and rupture of linear macromolecules in dilute solutions under the influence of viscous flow. <i>Chem. Abs.</i> , <u>39</u> , 1340 (1945)

REFERENCES (concluded)

- | <u>No.</u> | <u>Author</u>                             | <u>Title, etc.</u>   |
|------------|---|--|
| 103        | L.S. Churakova<br>A.A. Trapeznikov        | Anomalies of deformation-strength properties of a polyisobutylene solution in the intermediate range of deformation rates.<br><i>Chem. Abs.</i> , <u>78</u> , 125015a (1973) |
| 104        | T. Fukutomi<br>T. Kakurai<br>K. Yoshikawa | Effect of the solvent at various polymer concentrations on the mechanical scission of polymers in solutions.<br><i>Chem. Abs.</i> , <u>81</u> , 64135c (1974)                |
| 105        | G.V. Fedotov<br>A.A. Trapeznikov          | Work of mechanical degradation of a polymer in solution and effect of the rate of deformation on it.<br><i>Chem. Abs.</i> , <u>77</u> , 140675p (1972)                       |
| 106        | F. Bueche                                 | Mechanical degradation of high polymers.<br><i>J. Appl. Polym. Sci.</i> , <u>4</u> , 101 (1960)  |

Overall security classification of this page

UNLIMITED

As far as possible this page should contain only unclassified information. If it is necessary to enter classified information, the box above must be marked to indicate the classification, e.g. Restricted, Confidential or Secret.

1. DRIC Reference (to be added by DRIC)	2. Originator's Reference RAE TR 76073	3. Agency Reference N/A	4. Report Security Classification/Marking UNLIMITED	
5. DRIC Code for Originator 850186	6. Originator (Corporate Author) Name and Location Royal Aircraft Establishment, Farnborough, Hants., UK			
5a. Sponsoring Agency's Code N/A	6a. Sponsoring Agency (Contract Authority) Name and Location N/A			
7. Title Mechanical shear degradation of polymers in solution: a review				
7a. (For Translations) Title in Foreign Language				
7b. (For Conference Papers) Title, Place and Date of Conference				
8. Author 1. Surname, Initials Knight, J.	9a. Author 2	9b. Authors 3, 4, ...	10. Date June 1976	Pages 32 Refs. 106
11. Contract Number N/A	12. Period N/A	13. Project	14. Other Reference Nos. Mat 291	
15. Distribution statement (a) Controlled by - (b) Special limitations (if any) -				
16. Descriptors (Keywords) (Descriptors marked * are selected from TEST) Shear degradation, Polymers.				
17. Abstract  A review is given of the breakdown of polymers in solution caused by the application of mechanical shear energy. The characteristics of different degrading devices are mentioned together with the factors which determine the rate and extent of breakdown. The energetics and possible mechanisms of degradation are discussed. Finally, a more critical overall view is given of the results in order to list the conclusions which can be supported by the majority of evidence.				